

**Cosmetic composition comprising a polymer**

The present invention relates to a cosmetic composition comprising a particular polymer and intended for application to the skin of human beings.

5           The composition according to the invention may be a makeup composition or a care composition for the skin, and preferably a makeup composition.

          The makeup composition may be a foundation, an eyeshadow, a blusher, a concealer, an eyeliner or a  
10 body makeup product. More especially, the invention relates to a foundation composition.

          The care composition may be a face and body skincare product, in particular a sun product, or a skin colouring product (such as a self-tanning  
15 product).

          Foundation compositions are commonly used to give the skin, in particular the face, an aesthetic colour. These makeup products generally contain oils, pigments and/or fillers and optionally additives, such  
20 as cosmetic or dermatological actives.

          These compositions, when they are applied to the skin, exhibit the disadvantage of transferring, i.e. of undergoing at least partial deposition, leaving marks, on certain substrates with which they may be  
25 contacted, and in particular a glass, cup, cigarette, item of clothing, or the skin. A consequence of this is mediocre persistence of the applied film, making it

necessary regularly to renew the application of the lipstick or foundation composition. Moreover, the appearance of these unacceptable marks, particularly on blouse collars, may put certain women off using this  
5 type of makeup.

Furthermore, the sebum excreted by the skin over the course of time also alters the properties of the makeup. In particular, sebum does not promote the adhesion of the makeup to the skin, and the transfer of  
10 the makeup is even greater, giving rise to a substantial loss of the makeup remaining on the skin.

"Transfer-free" skin makeup compositions are therefore sought which exhibit the advantage of forming a transfer-resistant deposit, especially in the  
15 presence of sebum, and especially compositions which do not undergo at least partial deposition onto substrates with which they are contacted (glass, clothing, cigarettes, fabrics).

For the purpose of enhancing the persistence  
20 of makeup products the use of film-forming polymers is known. For example, documents US 6,074,654 and WO 02/067877 propose the use of silicone resins.

It is therefore an object of the present invention to provide a new formulation pathway for a  
25 cosmetic product which enables good transfer resistance properties to be obtained, especially in the presence of sebum.

The inventors have discovered that it is possible to obtain such a composition by using a particular polymer.

More specifically, therefore, the present invention provides a makeup or skincare cosmetic composition comprising a dispersion of particles, preferably solid particles, of a grafted ethylenic polymer in a liquid fatty phase as described below, the composition being in particular as defined below.

Advantageously the grafted ethylenic polymer is such that, when it is present in sufficient quantity in the composition, that composition is capable of forming a deposit having a transfer index in the presence of sebum of less than 4.

The invention also provides a method of making up the skin which comprises applying to the keratin materials, in particular to the skin, a composition as defined above.

The invention further provides for the use of a composition as defined above for obtaining a deposit, in particular a makeup deposit, on the skin that has good transfer resistance, especially in the presence of sebum.

The invention additionally provides for the use, in a cosmetic composition, of a dispersion of particles (preferably solid particles) of a grafted ethylenic polymer in dispersion in a liquid fatty

phase, the composition being capable in particular of forming a deposit having a transfer index in the presence of sebum of less than 4, for obtaining a deposit, in particular a makeup deposit, on the skin that exhibits good transfer resistance, especially in the presence of sebum.

Advantageously the grafted ethylenic polymer used in the composition according to the invention is such that, when it is present in sufficient quantity in the composition, that composition is capable of forming a deposit having a transfer index in the presence of sebum of less than 4, in particular less than or equal to 3.5, preferably less than or equal to 3, in particular less than or equal to 2.5, preferentially less than or equal to 2, more preferentially less than or equal to 1.5, and in particular less than or equal to 1.

The transfer index in the presence of sebum of the deposit obtained with the composition according to the invention is determined in accordance with the measuring protocol described below.

A substrate (square of 40 mm × 40 mm) composed of a layer of neoprene foam which is adhesive on one of its faces (sold under the name RE70X40 212B from Joint Technique Lyonnais Ind) is prepared. An adhesive crown having an internal diameter of 24 mm and a thickness of approximately 250 µm is affixed to the

non-adhesive face of the substrate. The composition is applied inside the crown and is levelled off with a glass slide so as to give a deposit of the composition approximately 250  $\mu\text{m}$  thick, and then the crown is withdrawn and the deposit is left to dry in an oven at 37°C for 20 hours.

The substrate is subsequently bonded by its adhesive face to an endpiece with a diameter of 27 mm which is fixed on a press (Statif Manuel SV-1 from Imada Co. Ltd.) which is equipped with a dynamometer (DPS-5R from Imada Co. Ltd.)

On a piece of photo-quality coated paper (reference Epson S041061, 102  $\text{g}/\text{m}^2$ ) a strip is drawn which is 4 cm wide and 21 cm long, and within this strip 5 boxes each 4.2 cm long are drawn along the longitudinal axis of the strip. The paper is placed on the bed of the press.

In the centre of the first box a drop of 10  $\mu\text{l}$  of artificial sebum is deposited, which has the following composition:

- triolein	29%
- oleic acid	28.5%
- oleyl oleate	18.5%
- squalene	14%
25 - cholesterol	7%
- cholesteryl palmitate	3%

The substrate (comprising the sample of

composition) is then pressed onto the first box of the paper strip, with a force of approximately 4 kg exerted for 5 seconds. The paper is then displaced in a regular, rectilinear fashion over the entire length of the strip, in such a way that the substrate is in contact with the entire length of the strip. The speed of displacement of the strip is of the order of 10 cm/s.

The trail of product deposited on the paper strip is then observed visually. A grade ranging from 0 to 5 in increments of 0.5 is awarded as a function of the number of boxes, from the first to the fifth, which have been traversed, where appropriate, completely or partly by the trail of product.

For certain products, without coloration, a visualization step may be necessary in order to make the trail of product visible. By way of example, a compound is used which is able to produce a coloured reaction on contact with the transferred product. According to another example, an active which emits in the visible range at least some of a UV radiation (Wood lamp) is incorporated into the product under test.

Grade 5 is awarded when, by observation, after the relative displacement between paper and substrate has taken place, there is substantially no product (less than 10%) remaining on the substrate. In this case, the transfer may be termed total.

Grade 5 is also awarded when the trail of product extends beyond the fifth box, independently of the amount of product remaining on the substrate.

Grade 0 is awarded when no product present on the support is transferred to the strip of paper. No visible trace can be observed on the sheet. The transfer may be termed zero.

By convention, the line of separation between box n and box n+1 forms part of box n.

The table below illustrates the way in which the other grades are awarded as a function of the point in boxes 1 to 5 at which the trail of product ends. For these grades, a larger or smaller amount of product remains on the substrate. The transfer is partial.

No. of the box at which the trail of product stops	Grade	
	More than half of the box	Up to half of the box
5	4.5	
		4
4	3.5	
		3
3	2.5	
		2
2	1.5	
		1
1	0.5	

The cosmetic composition according to the invention comprises a dispersion of particles, preferably solid particles, of a grafted ethylenic

polymer in a liquid fatty phase.

The cosmetic composition according to the invention is a composition which is compatible with keratin materials, and particularly with the skin.

5 By "ethylenic" polymer is meant a polymer obtained by polymerization of monomers comprising an ethylenic unsaturation.

The grafted ethylenic polymer dispersion is free in particular of stabilizing polymers other than  
10 the said grafted polymer, such as those described in EP 749 747, and the particles of grafted ethylenic polymer are therefore not surface-stabilized by such additional stabilizing polymers. The grafted polymer is therefore dispersed in the liquid fatty phase in the  
15 absence of additional stabilizer on the surface of the particles of the grafted polymer.

By grafted polymer is meant a polymer having a skeleton comprising at least one side chain which is pendent or situated at the chain end, preferably  
20 pendent.

Advantageously, the grafted ethylenic polymer comprises an ethylenic skeleton which is insoluble in the said liquid fatty phase, and side chains bonded covalently to the said skeleton and soluble in the said  
25 dispersion medium.

The grafted ethylenic polymer is in particular a non-crosslinked polymer. In particular,



the polymer is obtained by polymerizing monomers containing a single polymerizable moiety.

Preferably, the grafted ethylenic polymer is a film-forming polymer.

5 By "film-forming" polymer is meant a polymer suitable for forming, on its own or in the presence of an auxiliary film-forming agent, a continuous film which adheres to a substrate, particularly to keratin materials.

10 According to one embodiment of the invention, the grafted ethylenic polymer is a grafted acrylic polymer.

The grafted ethylenic polymer is obtainable in particular by free-radical polymerization in an  
15 organic polymerization medium:

- of at least one ethylenic monomer, in particular at least one acrylic monomer and, optionally, at least one additional, non-acrylic, vinyl monomer, to form the said insoluble skeleton; and
- 20 - of at least one macromonomer containing a polymerizable end group for forming side chains, the said macromonomer having a weight-average molecular mass of greater than or equal to 200, the amount of polymerized macromonomer representing from 0.05% to 20%  
25 by weight of the polymer.

The liquid fatty phase may contain the organic polymerization medium.

The liquid organic dispersion medium, corresponding to the medium in which the grafted polymer is provided, may be identical to the polymerization medium.

5                However, the polymerization medium may be wholly or partly substituted by another liquid organic medium. This other liquid organic medium may be added after polymerization to the polymerization medium. The latter is then wholly or partly evaporated.

10              The liquid fatty phase may comprise organic liquid compounds other than those present in the dispersion medium. These other compounds are selected such that the grafted polymer remains in the state of dispersion in the liquid fatty phase.

15              The organic liquid dispersion medium is present in the liquid fatty phase of the composition according to the invention owing to the introduction of the grafted polymer dispersion obtained into the composition.

20              The liquid fatty phase comprises, preferably on a majority basis, one or more liquid organic compounds (or oils) as defined below.

                In particular, the liquid fatty phase is a liquid organic phase which is non-aqueous and water-  
25 immiscible at ambient temperature (25°C).

                A "liquid organic compound" is a non-aqueous compound which is in the liquid state at ambient

temperature (25°C) and which therefore flows under its own weight.

A "silicone compound" is a compound containing at least one silicon atom.

5           Among the liquid organic compounds or oils, in particular volatile or non-volatile, that may be present in the liquid organic dispersion medium, mention may be made of:

- liquid organic compounds, especially silicone-based  
10 or non-silicone-based, having a total solubility parameter according to the Hansen solubility space of less than or equal to  $18 \text{ (MPa)}^{1/2}$  and preferably less than or equal to  $17 \text{ (MPa)}^{1/2}$ ,
- monoalcohols having a total solubility parameter  
15 according to the Hansen solubility space of less than or equal to  $20 \text{ (MPa)}^{1/2}$ , and
- mixtures thereof.

The total solubility parameter  $\delta$  according to the Hansen solubility space is defined in the article  
20 "Solubility parameter values" by Eric A. Grulke in the work "Polymer Handbook", 3rd Edition, Chapter VII, p. 519-559, by the relationship:

$$\delta = (d_D^2 + d_P^2 + d_H^2)^{1/2}$$

in which

- 25 -  $d_D$  characterizes the London dispersion forces arising from the formation of dipoles induced during molecular impacts,

- $d_p$  characterizes the Debye interaction forces between permanent dipoles, and
- $d_H$  characterizes the forces of specific interactions (such as hydrogen bonding, acid/base, donor/acceptor, etc.).

The definition of solvents in the solubility space according to Hansen is described in the article by C. M. Hansen: "The three dimensional solubility parameters", J. Paint Technol. 39, 105 (1967).

Among the liquid organic compounds, especially silicone-based or non-silicone-based, having a total solubility parameter according to the Hansen solubility space of less than or equal to  $18 \text{ (MPa)}^{1/2}$ , mention may be made of liquid fatty substances, especially oils, which may be selected from natural or synthetic, carbon-based, hydrocarbon-based, fluoro and silicone oils, which are optionally branched, alone or as a mixture.

An "oil" is any non-aqueous medium which is liquid at ambient temperature ( $25^\circ\text{C}$ ) and atmospheric pressure (760 mmHg) and is compatible with application to the skin, mucosae (lips) and/or epidermal derivatives (nails, eyebrows, eyelashes, hair).

Among these oils, mention may be made of plant oils formed from fatty acid esters and from polyols, in particular triglycerides, such as sunflower oil, sesame oil or rapeseed oil, or esters derived from

acids or alcohols containing a long chain (i.e. a chain containing from 6 to 20 carbon atoms), in particular the esters of formula  $\text{RCOOR}'$  in which R represents a higher fatty acid residue containing from 7 to 19

5 carbon atoms and  $\text{R}'$  represents a hydrocarbon-based chain containing from 3 to 20 carbon atoms, such as palmitates, adipates and benzoates, in particular diisopropyl adipate.

Mention may also be made of linear, branched  
10 and/or cyclic alkanes which may be volatile, and in particular liquid paraffin, liquid petroleum jelly or hydrogenated polyisobutylene, isododecane or "Isopars", volatile isoparaffins. Mention may also be made of esters, ethers and ketones.

15 Mention may also be made of silicone oils such as polydimethylsiloxanes and polymethylphenylsiloxanes, optionally substituted with aliphatic and/or aromatic groups, which are optionally fluorinated, or with functional groups such as hydroxyl, thiol and/or  
20 amine groups, and volatile silicone oils, which are especially cyclic.

In particular, mention may be made of volatile and/or non-volatile, optionally branched silicone oils.

25 The term "volatile oil" means any non-aqueous medium capable of evaporating from the skin or the lips in less than one hour, and especially having a vapour

pressure, at ambient temperature and atmospheric pressure, ranging from  $10^{-3}$  to 300 mmHg (0.13 Pa to 40 000 Pa).

As volatile silicone oils that may be used in the invention, mention may be made of linear or cyclic silicones containing from 2 to 7 silicon atoms, these silicones optionally comprising alkyl or alkoxy groups containing from 1 to 10 carbon atoms. Mention may be made in particular of octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, heptamethylhexyltrisiloxane, heptamethyloctyltrisiloxane, octamethyltrisiloxane and decamethyltetrasiloxane, and mixtures thereof.

Among the non-volatile silicone oils that may be mentioned are non-volatile polydialkylsiloxanes, such as non-volatile polydimethylsiloxanes (PDMS); polydimethylsiloxanes comprising alkyl, alkoxy or phenyl groups, which are pendent or at the end of a silicone chain, these groups containing from 2 to 24 carbon atoms; phenyl silicones, for instance phenyl trimethicones, phenyl dimethicones, phenyl trimethylsiloxyl diphenylsiloxanes, diphenyl dimethicones, diphenyl methyldiphenyltrisiloxanes and polymethylphenylsiloxanes; polysiloxanes modified with fatty acids (especially of  $C_8$ - $C_{20}$ ), fatty alcohols (especially of  $C_8$ - $C_{20}$ ) or polyoxyalkylenes (especially polyoxyethylene and/or polyoxypropylene); amino polysiloxanes;

polysiloxanes containing hydroxyl groups; fluoro polysiloxanes comprising a fluorinated group that is pendent or at the end of a silicone chain, containing from 1 to 12 carbon atoms, all or some of the hydrogens of which are substituted by fluorine atoms; and mixtures thereof.

As non-silicone-based liquid organic compounds with a total solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)<sup>1/2</sup>, mention may be made in particular of:

- linear, branched or cyclic esters containing at least 6 carbon atoms, especially 6 to 30 carbon atoms;
- ethers containing at least 6 carbon atoms, especially 6 to 30 carbon atoms; and
- ketones containing at least 6 carbon atoms, especially 6 to 30 carbon atoms.

The expression "liquid monoalcohols having a total solubility parameter according to the Hansen solubility space of less than or equal to 20 (MPa)<sup>1/2</sup>" means aliphatic fatty liquid monoalcohols containing from 6 to 30 carbon atoms, the hydrocarbon-based chain not comprising a substitution group. Monoalcohols according to the invention that may be mentioned include oleyl alcohol, decanol and linoleyl alcohol.

Advantageously, the composition according to the invention may comprise a volatile oil in an amount ranging from 1% to 90% by weight, relative to the total

weight of the composition, and preferably ranging from 5% to 70% by weight.

The composition may comprise a non-volatile oil in an amount ranging from 0.1% to 80% by weight, relative to the total weight of the composition, and preferably ranging from 3% to 50% by weight.

According to a first embodiment of the invention, the liquid fatty phase may be a non-silicone-based liquid fatty phase.

The term "non-silicone-based liquid fatty phase" means a fatty phase comprising one or more non-silicone-based liquid organic compound(s) or oil(s), such as those mentioned above, the said non-silicone compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or alternatively from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

The non-silicone-based liquid organic compounds may especially be selected from:

- non-silicone-based liquid organic compounds having a total solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)<sup>1/2</sup>,
- monoalcohols having a total solubility parameter according to the Hansen solubility space of less than



or equal to 20 (MPa)<sup>1/2</sup>; and

- mixtures thereof.

The said non-silicone-based liquid fatty phase may thus optionally comprise silicone-based liquid organic compounds or oils, such as those mentioned previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or alternatively ranging from 5% to 30% by weight, relative to the total weight of the liquid fatty phase.

According to one particular embodiment of the invention, the non-silicone-based liquid fatty phase does not contain any silicone-based liquid organic compounds or oils.

When the liquid fatty phase is a non-silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously carbon-based macromonomers as described below.

The term "non-silicone-based grafted polymer" means a grafted polymer predominantly containing a carbon-based macromonomer and optionally containing not more than 7% by weight of the total weight of the polymer, and preferably not more than 5% by weight, of silicone macromonomer, or even being free of silicone macromonomer.

According to a second embodiment of the

invention, the liquid fatty phase may be a silicone-based liquid fatty phase.

The term "silicone-based liquid fatty phase" means a fatty phase comprising one or more silicone-based liquid organic compound(s) or silicone oil(s) such as those described previously, the said silicone compounds being predominantly present in the liquid fatty phase, i.e. to at least 50% by weight, especially from 50% to 100% by weight, preferably from 60% to 100% by weight (for example from 60% to 99% by weight), or even from 65% to 100% by weight (for example from 65% to 95% by weight), relative to the total weight of the liquid fatty phase.

The silicone-based liquid organic compounds may especially be selected from:

- liquid organic compounds, which are especially non-silicone-based or silicone-based, with a total solubility parameter according to the Hansen solubility space of less than or equal to 18 (MPa)<sup>1/2</sup>.

The said silicone-based liquid fatty phase may thus optionally comprise non-silicone-based liquid organic compounds or oils, as described previously, which may be present in an amount of less than 50% by weight, especially ranging from 0.1% to 40% by weight, or even ranging from 1% to 35% by weight, or else ranging from 5% to 30% by weight, relative to the total weight of the liquid fatty phase.

According to one particular embodiment of the invention, the silicone-based liquid fatty phase contains no non-silicone-based liquid organic compounds.

5           When the liquid fatty phase is a silicone-based liquid fatty phase, the macromonomers present in the grafted polymer are advantageously silicone-based macromonomers as described below.

          In particular, when the liquid fatty phase is  
10 a silicone-based liquid fatty phase, the grafted polymer present in the composition is advantageously a silicone-based grafted polymer.

          The term "silicone-based grafted polymer" means a grafted polymer predominantly containing a  
15 silicone-based macromonomer optionally containing up to 7% by weight of the total weight of the polymer, and preferably up to 5% by weight, of carbon-based macromonomer, or even being free of carbon-based macromonomer.

20           The choice of monomers constituting the skeleton of the polymer, of macromonomers, the molecular weight of the polymer, and the proportion of the monomers and macromonomers may be made as a function of the liquid organic dispersion medium so as  
25 advantageously to obtain a dispersion of particles of grafted polymers, in particular a stable dispersion, this choice possibly being made by a person skilled in

the art.

The term "stable dispersion" means a dispersion that is not liable to form a solid deposit or to undergo liquid/solid phase separation, especially  
5 after centrifugation, for example, at 4000 rpm for 15 minutes.

The grafted ethylenic polymer forming the particles in dispersion thus comprises a skeleton that is insoluble in the said dispersion medium and a  
10 portion that is soluble in the said dispersion medium.

The grafted ethylenic polymer may be a random polymer.

According to the invention, the term "grafted ethylenic polymer" means a polymer obtainable by  
15 free-radical polymerization:

- of one or more ethylenic monomer(s),
- with one or more macromonomer(s), in an organic polymerization medium.

According to the invention, a "grafted  
20 acrylic polymer" is a polymer obtainable by free-radical polymerization:

- of one or more acrylic monomers and, optionally, one or more additional non-acrylic vinyl monomers,
- with one or more macromonomers in an organic  
25 polymerization medium.

Advantageously, the acrylic monomers represent from 50% to 100% by weight, preferably from

55% to 100% by weight (in particular from 55% to 95% by weight), preferentially from 60% to 100% by weight (in particular from 60% to 90% by weight) of the mixture of acrylic monomers + optional non-acrylic vinyl monomers.

5            Preferably, the acrylic monomers are selected from monomers whose homopolymer is insoluble in the dispersion medium under consideration, i.e. the homopolymer is in solid (or non-dissolved) form at a concentration of greater than or equal to 5% by weight  
10 at ambient temperature (20°C) in the said dispersion medium.

          According to the invention, the expression "macromonomer containing a polymerizable end group" means any polymer comprising on only one of its ends a  
15 polymerizable end group capable of reacting during the polymerization reaction with acrylic monomers and optionally the additional non-acrylic vinyl monomers constituting the skeleton. The macromonomer makes it possible to form the side chains of the grafted acrylic  
20 polymer. The polymerizable group of the macromonomer may advantageously be an ethylenically unsaturated group capable of free-radical polymerization with the monomers constituting the skeleton.

          The term "carbon-based macromonomer" means a  
25 non-silicone-based macromonomer and especially an oligomeric macromonomer obtained by polymerization of ethylenically unsaturated non-silicone-based

monomer(s), and mainly by polymerization of acrylic and/or non-acrylic vinyl monomers.

The term "silicone-based macromonomer" means an organopolysiloxane macromonomer and in particular a  
5 polydimethylsiloxane macromonomer.

Preferably, the macromonomer is selected from macromonomers whose homopolymer is soluble in the dispersion medium under consideration, i.e. fully dissolved at a concentration of greater than or equal  
10 to 5% by weight and at ambient temperature in the said dispersion medium.

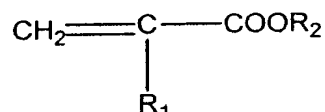
Thus, the grafted acrylic polymer comprises a skeleton (or main chain) consisting of a sequence of acrylic units resulting from the polymerization  
15 especially of one or more acrylic monomers and of side chains (or grafts) derived from the reaction of the macromonomers, the said side chains being covalently bonded to the said main chain.

The skeleton (or main chain) is insoluble in  
20 the dispersion medium under consideration, whereas the side chains (or grafts) are soluble in the said dispersion medium.

In the present patent application, the term "acrylic monomers" means monomers selected from  
25 (meth)acrylic acid, (meth)acrylic acid esters (also known as (meth)acrylates), and (meth)acrylic acid amides (also known as (meth)acrylamides).

As acrylic monomers that may be used to form the insoluble skeleton of the polymer, mention may be made, alone or as a mixture, of the following monomers, and also the salts thereof:

- 5    -(i) the (meth)acrylates of formula:



in which:

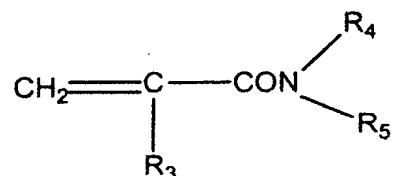
- $\text{R}_1$  denotes a hydrogen atom or a methyl group;
- $\text{R}_2$  represents a group selected from:
  - 10               - a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group possibly comprising in its chain one or more heteroatoms selected from O, N and S; and/or possibly comprising one or more substituents selected from -OH, halogen
  - 15               atoms (F, Cl, Br or I) and -NR'R'' with R' and R'', which may be identical or different, selected from linear or branched  $\text{C}_1$ - $\text{C}_4$  alkyls; and/or possibly being substituted with at least one polyoxyalkylene group, in particular with  $\text{C}_2$ - $\text{C}_4$  alkylene, especially polyoxyethylene and/or
  - 20               polyoxypropylene, the said polyoxyalkylene group consisting of a repetition of 5 to 30 oxyalkylene units;
  - a cyclic alkyl group containing from 3 to 6 carbon atoms, the said group possibly comprising in its
  - 25               chain one or more heteroatoms selected from O, N and S, and/or possibly comprising one or more substituents

selected from OH and halogen atoms (F, Cl, Br or I).

Examples of  $R_2$  that may be mentioned include the methyl, ethyl, propyl, butyl, isobutyl, methoxyethyl, ethoxyethyl, methoxypolyoxyethylene

5 (350 EO), trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl or dimethylaminopropyl group;

-(ii) the (meth)acrylamides of formula:



10 in which:

- $R_3$  denotes a hydrogen atom or a methyl group;
- $R_4$  and  $R_5$ , which may be identical or different, represent a hydrogen atom or a linear or branched alkyl group containing from 1 to 6 carbon atoms, which may
- 15 comprise one or more substituents selected from -OH, halogen atoms (F, Cl, Br or I) and -NR'R'' with R' and R'', which may be identical or different, selected from linear or branched  $C_1$ - $C_4$  alkyls; or
- $R_4$  represents a hydrogen atom and  $R_5$  represents a
- 20 1,1-dimethyl-3-oxobutyl group.

As examples of alkyl groups that can constitute  $R_4$  and  $R_5$ , mention may be made of n-butyl, t-butyl, n-propyl, dimethylaminoethyl, diethylaminoethyl and dimethylaminopropyl.



-(iii) (meth)acrylic monomers comprising at least one carboxylic, phosphoric or sulfonic acid function, such as acrylic acid, methacrylic acid and acrylamido-propanesulfonic acid.

5           Among these acrylic monomers, those that may be mentioned most particularly are methyl, ethyl, propyl, butyl and isobutyl (meth)acrylates; methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl  
10 methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl acrylate; dimethylaminopropylmethacrylamide; (meth)acrylic acid; and the salts thereof; and mixtures  
15 thereof.

          Preferably, the acrylic monomers are selected from methyl acrylate, methoxyethyl acrylate, methyl methacrylate, 2-hydroxyethyl methacrylate, (meth)acrylic acid and dimethylaminoethyl methacrylate,  
20 and mixtures thereof.

          Among the additional non-acrylic vinyl monomers that may be mentioned are:  
- vinyl esters of formula:  $R_6\text{-COO-CH=CH}_2$   
in which  $R_6$  represents a linear or branched alkyl group  
25 containing from 1 to 6 carbon atoms, or a cyclic alkyl group containing from 3 to 6 carbon atoms and/or an aromatic group, for example of benzene, anthracene or

naphthalene type;

- non-acrylic vinyl monomers comprising at least one carboxylic, phosphoric or sulfonic acid function, such as crotonic acid, maleic anhydride, itaconic acid, fumaric acid, maleic acid, styrenesulfonic acid, vinylbenzoic acid, vinylphosphoric acid, and salts thereof;
- non-acrylic vinyl monomers comprising at least one tertiary amine function, such as 2-vinylpyridine or 4-vinylpyridine;
- and mixtures thereof.

According to one embodiment of the invention, the grafted polymer comprises (meth)acrylic acid.

Advantageously, the acrylic monomers present in the grafted polymer comprise at least (meth)acrylic acid, and in particular at least (meth)acrylic acid and at least one monomer selected from the (meth)acrylates and the (meth)acrylamides described above in sections (i) and (ii). Preferably, the acrylic monomers comprise at least (meth)acrylic acid and at least one monomer selected from C<sub>1</sub>-C<sub>3</sub> alkyl (meth)acrylates. (Meth)acrylic acid may be present in an amount of at least 5% by weight, relative to the total weight of the polymer (in particular ranging from 5% to 80% by weight), preferably of at least 10% by weight (in particular ranging from 10% by weight to 70% by weight), preferentially of at least 15% by weight (in particular

ranging from 15% to 60% by weight).

Among the salts, those that may be mentioned are those obtained by neutralization of acidic moieties with inorganic bases such as sodium hydroxide,

5 potassium hydroxide or ammonium hydroxide, or organic bases such as alkanolamines, for instance monoethanolamine, diethanolamine, triethanolamine or 2-methyl-2-amino-1-propanol.

Mention may also be made of the salts formed  
10 by neutralization of tertiary amine units, for example using a mineral or organic acid. Among the mineral acids that may be mentioned are sulfuric acid, hydrochloric acid, hydrobromic acid, hydriodic acid, phosphoric acid and boric acid. Among the organic acids  
15 that may be mentioned are acids comprising one or more carboxylic, sulfonic or phosphonic groups. They may be linear, branched or cyclic aliphatic acids, or alternatively aromatic acids. These acids may also comprise one or more heteroatoms selected from O and N,  
20 for example in the form of hydroxyl groups. Acetic acid or propionic acid, terephthalic acid, and citric acid and tartaric acid may especially be mentioned.

According to one embodiment of the invention, the grafted acrylic polymer contains no additional non-  
25 acrylic vinyl monomers as described above. In this embodiment, the insoluble skeleton of the grafted ethylenic polymer is formed solely from acrylic

monomers as described previously.

It is understood that these non-polymerized acrylic monomers may be soluble in the dispersion medium under consideration, but the polymer formed with  
5 these monomers is insoluble in the dispersion medium.

According to one particular embodiment of the invention, the grafted ethylenic polymer is obtainable by free-radical polymerization in an organic polymerization medium:

- 10 - of a principal acrylic monomer selected from  $C_1$ - $C_3$  alkyl (meth)acrylates, alone or in a mixture, and, optionally, of one or more additional acrylic monomers selected from acrylic acid, methacrylic acid and the alkyl (meth)acrylates of formula (I) defined below, and  
15 salts thereof, to form the said insoluble skeleton; and  
- of at least one silicone-based macromonomer comprising a polymerizable end group, as defined above.

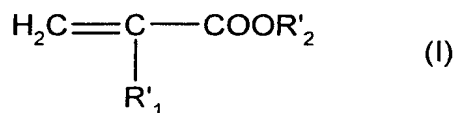
As main acrylic monomer it is possible to use methyl acrylate, methyl methacrylate, ethyl acrylate,  
20 ethyl methacrylate, n-propyl acrylate, n-propyl methacrylate, isopropyl acrylate and isopropyl methacrylate, and mixtures thereof.

Very particular preference is given to methyl acrylate, methyl methacrylate and ethyl methacrylate.

25 The additional acrylic monomers may be selected from:

- (meth)acrylic acid and its salts,

- the (meth)acrylates of formula (I) and their salts:



in which:

- R'<sub>1</sub> denotes a hydrogen atom or a methyl group;
- 5 - R'<sub>2</sub> represents
  - a linear or branched alkyl group containing from 1 to 6 carbon atoms, the said group comprising in its chain one or more oxygen atoms and/or comprising one or more substituents selected from
  - 10 -OH, halogen atoms (F, Cl, Br, I) and -NR'R'', where R' and R'' are identical or different and selected from linear or branched C<sub>1</sub>-C<sub>3</sub> alkyls;
  - a cyclic alkyl group containing from 3 to 6 carbon atoms, it being possible for the said group to
  - 15 comprise in its chain one or more oxygen atoms and/or to comprise one or more substituents selected from OH and halogen atoms (F, Cl, Br, I);
  - and mixtures thereof.

Possible examples of R'<sub>2</sub> include the group

20 methoxyethyl, ethoxyethyl, trifluoroethyl; 2-hydroxyethyl, 2-hydroxypropyl, dimethylaminoethyl, diethylaminoethyl, dimethylaminopropyl.

Among these additional acrylic monomers mention may be made very particularly of (meth)acrylic

25 acid, methoxyethyl or ethoxyethyl (meth)acrylates; trifluoroethyl methacrylate; dimethylaminoethyl

methacrylate, diethylaminoethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxyethyl acrylate, salts thereof, and mixtures thereof.

5           Very particular preference is given to acrylic acid, methylacrylic acid.

          The macromonomers comprise at one of the ends of the chain a polymerizable end group capable of reacting during the polymerization with the acrylic  
10 monomers and optionally the additional vinyl monomers, to form the side chains of the grafted ethylenic polymer. The said polymerizable end group may in particular be a vinyl or (meth)acrylate (or (meth)acryloyl) group, and preferably a (meth)acrylate  
15 group.

          The macromonomers are preferably selected from macromonomers whose homopolymer has a glass transition temperature ( $T_g$ ) of less than or equal to  $25^\circ\text{C}$ , especially ranging from  $-100^\circ\text{C}$  to  $25^\circ\text{C}$  and  
20 preferably ranging from  $-80^\circ\text{C}$  to  $0^\circ\text{C}$ .

          The macromonomers have a weight-average molecular mass of greater than or equal to 200, preferably greater than or equal to 300, preferentially greater than or equal to 500 and more preferentially  
25 greater than 600.

          Preferably, the macromonomers have a weight-average molecular mass ( $M_w$ ) ranging from 200 to

100 000, preferably ranging from 500 to 50 000,  
preferentially ranging from 800 to 20 000, more  
preferentially ranging from 800 to 10 000 and even more  
preferentially ranging from 800 to 6000.

5           In the present patent application, the  
weight-average (Mw) and number-average (Mn) molar  
masses are determined by liquid gel permeation  
chromatography (THF solvent, calibration curve  
established with linear polystyrene standards,  
10 refractometric detector).

Carbon-based macromonomers that may in  
particular be mentioned include:

-(i) homopolymers and copolymers of linear or branched  
C<sub>8</sub>-C<sub>22</sub> alkyl (meth)acrylate, containing a polymerizable  
15 end group selected from vinyl or (meth)acrylate groups,  
among which mention may be made in particular of:  
poly(2-ethylhexyl acrylate) macromonomers with a  
mono(meth)acrylate end group; poly(dodecyl acrylate) or  
poly(dodecyl methacrylate) macromonomers with a  
20 mono(meth)acrylate end group; poly(stearyl acrylate) or  
poly(stearyl methacrylate) macromonomers with a  
mono(meth)acrylate end group.

Such macromonomers are described in  
particular in the patents EP 895 467 and EP 96 459, and  
25 in the article by Gillman K.F., Polymer Letters, Vol 5,  
pages 477-481 (1967).

Mention may be made in particular of

macromonomers based on poly(2-ethylhexyl acrylate) or poly(dodecyl acrylate) with a mono(meth)acrylate end group;

- 5       -(ii) polyolefins containing an ethylenically unsaturated end group, in particular containing a (meth)acrylate end group. Examples of such polyolefins that may be mentioned in particular include the following macromonomers, it being understood that they have a (meth)acrylate end group: polyethylene
- 10   macromonomers, polypropylene macromonomers, macromonomers of polyethylene/polypropylene copolymer, macromonomers of polyethylene/polybutylene copolymer, polyisobutylene macromonomers; polybutadiene macromonomers; polyisoprene macromonomers;
- 15   polybutadiene macromonomers; poly(ethylene/butylene)-polyisoprene macromonomers.

Such macromonomers are described in particular in US 5,625,005, which mentions ethylene/butylene and ethylene/propylene macromonomers

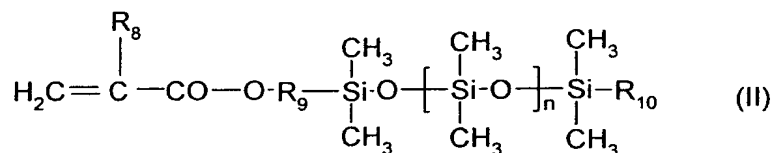
20   containing a (meth)acrylate reactive end group.

Mention may be made in particular of the poly(ethylene/butylene) methacrylate such as that sold under the name Kraton Liquid L-1253 by Kraton Polymers.

Silicone-based macromonomers that may be

25   mentioned in particular include polydimethylsiloxanes with a mono(meth)acrylate end group, and especially those of formula (II) below:





in which  $\text{R}_8$  denotes a hydrogen atom or a methyl group;  
 $\text{R}_9$  denotes a divalent hydrocarbon-based group containing  
 from 1 to 10 carbon atoms and optionally contains one  
 5 or two ether bonds  $-\text{O}-$ ;  $\text{R}_{10}$  denotes an alkyl group  
 containing from 1 to 10 carbon atoms and especially  
 from 2 to 8 carbon atoms;  $n$  denotes an integer ranging  
 from 1 to 300, preferably ranging from 3 to 200 and  
 preferentially ranging from 5 to 100.

10           Silicone-based macromonomers that may be used  
 include monomethacryloxypropyl polydimethylsiloxanes  
 such as those sold under the name PS560-K6 by the  
 company United Chemical Technologies Inc. (UCT) or  
 under the name MCR-M17 by the company Gelest Inc.

15           Preferably, the polymerized macromonomer  
 (constituting the side chains of the grafted polymer)  
 represents from 0.1% to 15% by weight of the total  
 weight of the polymer, preferably from 0.2% to 10% by  
 weight and more preferably from 0.3% to 8% by weight.

20           As particularly preferred grafted ethylenic  
 polymer dispersed in a non-silicone-based liquid fatty  
 phase, it is possible to use those obtained by  
 polymerization:

- of methyl acrylate and of a polyethylene/polybutylene  
 25 macromonomer with a methacrylate end group (especially

Kraton L-1253), in particular in a solvent selected from isododecane, isononyl isononanoate, octyldodecanol, diisostearyl malate and a C<sub>12</sub>-C<sub>15</sub> alkyl benzoate (such as Finsolv TN);

- 5 - of methoxyethyl acrylate and of a polyethylene/polybutylene macromonomer with a methacrylate end group (especially Kraton L-1253), in particular in isododecane;
- of methyl acrylate/methyl methacrylate monomers and
- 10 of a polyethylene/polybutylene macromonomer with a methacrylate end group (especially Kraton L-1253), in particular in isododecane;
- of methyl acrylate/acrylic acid monomers and of a polyethylene/polybutylene macromonomer with a
- 15 methacrylate end group (especially Kraton L-1253), in particular in isododecane;
- of methyl acrylate/dimethylaminoethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer with a methacrylate end group (especially
- 20 Kraton L-1253), in particular in isododecane;
- of methyl acrylate/2-hydroxyethyl methacrylate monomers and of a polyethylene/polybutylene macromonomer with a methacrylate end group (especially Kraton L-1253), in particular in isododecane.

25           As particularly preferred grafted acrylic polymer dispersed in a silicone-based liquid fatty phase, it is possible to use those obtained by

polymerization:

- of methyl acrylate and of a monomethacryloyloxypropyl polydimethylsiloxane macromonomer with a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyltrimethicone;
- of methyl acrylate, acrylic acid and the monomethacryloyloxypropyl polydimethylsiloxane macromonomer with a weight-average molecular weight ranging from 800 to 6000, in particular in decamethylcyclopentasiloxane or phenyltrimethicone.

The weight-average molecular mass (Mw) of the grafted polymer is preferably between 10 000 and 300 000, especially between 20 000 and 200 000 and better still between 25 000 and 150 000.

By virtue of the abovementioned characteristics, in a given organic dispersion medium, the polymers have the capacity of folding over on themselves, thus forming particles of substantially spherical shape, the periphery of these particles having the deployed side chains, which ensure the stability of these particles. Such particles resulting from the characteristics of the grafted polymer have the particular feature of not agglomerating in the said medium and thus of being self-stabilized and of forming a particularly stable polymer particle dispersion.

In particular, the grafted ethylenic polymers

of the dispersion are capable of forming nanometre-sized particles, with a mean size ranging from 10 to 400 nm and preferably from 20 to 200 nm.

As a result of this very small size, the  
5 grafted polymer particles in dispersion are particularly stable and therefore have little susceptibility to form agglomerates.

The dispersion of grafted polymer may thus be a dispersion that is stable and does not form sediments  
10 when it is placed at ambient temperature (25°C) for an extended period (for example 24 hours).

Preferably, the dispersion of grafted polymer particles has a solids content (or dry extract) of polymer of from 40% to 70% by weight of solids and  
15 especially from 45% to 65% by weight.

The dispersion of grafted polymer particles may be prepared by a process comprising a free-radical copolymerization step, in an organic polymerization medium, of one or more acrylic monomers as defined  
20 above with one or more macromonomers as defined above.

As mentioned previously, the liquid organic dispersion medium may be identical to or different from the polymerization medium.

The copolymerization may be performed  
25 conventionally in the presence of a polymerization initiator. The polymerization initiators may be free-radical initiators. In general, such a polymerization

initiator may be selected from organic peroxide compounds such as dilauroyl peroxide, dibenzoyl peroxide or tert-butyl peroxy-2-ethylhexanoate; diazo compounds such as azobisisobutyronitrile or  
5 azobisdimethylvaleronitrile.

The reaction may also be initiated using photoinitiators or with radiation such as UV or neutrons, or with plasma.

In general, to perform this process, at least  
10 a portion of the organic polymerization medium, a portion of the additional acrylic and/or vinyl monomers, which will constitute the insoluble skeleton after polymerization, all of the macromonomer (which will constitute the side chains of the polymer) and a  
15 portion of the polymerization initiator are introduced into a reactor whose size is suitable for the amount of polymer to be prepared. At this stage of introduction, the reaction medium forms a relatively homogeneous medium.

20 The reaction medium is then stirred and heated up to a temperature to obtain polymerization of the monomers and macromonomers. After a certain time, the initially homogeneous and clear medium leads to a dispersion of milky appearance. A mixture consisting of  
25 the remaining portion of monomers and of polymerization initiator is then added. After an adequate time during which the mixture is heated with stirring, the medium

stabilizes in the form of a milky dispersion, the dispersion comprising polymer particles stabilized in the medium in which they have been created, the said stabilization being due to the presence, in the  
5 polymer, of side chains that are soluble in the said dispersion medium.

The grafted polymer described above may be present in the composition according to the invention in an amount ranging from 0.5% to 45% by weight  
10 relative to the total weight of the composition, preferably ranging from 1% to 30% by weight and preferentially ranging from 2% to 25% by weight.

The composition according to the invention may comprise one or more colorants selected from water-  
15 soluble dyes and pulverulent colorants such as pigments, nacles and flakes, which are well known to the person skilled in the art. The colorants may be present in the composition in an amount ranging from 0.01% to 50% by weight, relative to the weight of the  
20 composition, preferably from 0.01% to 30% by weight.

By pigments are meant white or coloured, mineral or organic particles of any form which are insoluble in the physiological medium and are intended for colouring the composition.

25 Nacles are irridescient particles of any form, produced in particular by certain molluscs within their shell, or else synthesized.

The pigments may be white or coloured, mineral and/or organic. Among mineral pigments mention may be made of titanium dioxide, optionally surface-treated, zirconium oxide or cerium oxide, and also zinc  
5 oxide, iron oxide (black, yellow or red) or chromium oxide, manganese violet, ultramarine blue, chromium hydrate and ferric blue, and metal powders such as aluminium powder and copper powder.

Among organic pigments mention may be made of  
10 carbon black, D & C pigments, and lakes based on cochineal carmine, barium, strontium, calcium and aluminium.

Mention may also be made of effect pigments, such as particles comprising an organic or mineral,  
15 natural or synthetic substrate, for example glass, acrylic resins, polyester, polyurethane, polyethylene terephthalate, ceramics or aluminas, the said substrate being bare or covered with metallic substances such as aluminium, gold, silver, platinum, copper, bronze, or  
20 with metal oxides such as titanium dioxide, iron oxide, chromium oxide and mixtures thereof.

The nacreous pigments may be selected from white nacreous pigments such as titanium-coated mica, or bismuth oxychloride, coloured nacreous pigments such  
25 as titanium mica coated with iron oxides, titanium mica coated with, in particular, ferric blue or chromium oxide, titanium mica coated with an organic pigment of

the aforementioned type, and also nacreous pigments based on bismuth oxychloride. Use may also be made of interference pigments, especially liquid-crystal pigments or multilayer pigments.

5                    Advantageously, the grafted polymer present in the composition according to the invention makes it possible to obtain a good, homogeneous dispersion of the pulverulent colorants such as the pigments or the nacles.

10                   The invention accordingly further provides a foundation composition comprising a dispersion of particles of grafted ethylenic polymer in a liquid fatty phase, as described above, and at least one colorant, especially pigments and nacles, or any other  
15                   filler having an optical effect.

                  The water-soluble dyes are, for example, beetroot juice and methylene blue.

                  The composition according to the invention may further comprise one or more fillers, in particular  
20                   in an amount ranging from 0.01% to 50% by weight, relative to the total weight of the composition, preferably ranging from 0.01% to 30% by weight. By fillers are meant particles of any shape, colourless or white, mineral or synthetic, which are insoluble in the  
25                   medium of the composition irrespective of the temperature at which the composition is manufactured. These fillers serve in particular to modify the



rheology or texture of the composition.

The fillers may be mineral or organic fillers of any form, platelet-like, spherical or oblong, irrespective of the crystallographic form (for example, 5 leaflet, cubic, hexagonal, orthorhombic, etc.). Mention may be made of talc, mica, silica, kaolin, polyamide (Nylon®) powders (Orgasol® from Atochem), poly- $\beta$ -alanine powders and polyethylene powders, powders of polymers of tetrafluoroethylene (Teflon®), lauroyllysine, 10 starch, boron nitride, hollow polymeric microspheres such as those of polyvinylidene chloride/acrylonitrile, for instance Expancel® (Nobel Industries), and of acrylic acid copolymers (Polytrap® from Dow Corning), and silicone resin microbeads (Tospearls® from Toshiba, 15 for example), particles of elastomeric organopolysiloxanes, precipitated calcium carbonate, magnesium carbonate and bicarbonate, hydroxyapatite, hollow silica microspheres (Silica Beads® from Maprecos), glass or ceramic microcapsules, metal soaps 20 derived from organic carboxylic acids having 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, for example zinc stearate, magnesium stearate or lithium stearate, zinc laurate and magnesium myristate.

The composition according to the invention 25 may further comprise ingredients commonly used in cosmetology, such as vitamins, moisturizers, emollients, free-radical scavengers, thickeners, trace

elements, softeners, sequesterants, perfumes, alkalifying or acidifying agents, preservatives, sunscreens, surfactants, antioxidants, gums, waxes, propellants, or mixtures thereof.

5           The person skilled in the art will of course take care to select this or these optional additional compounds, and/or their amount, such that the advantageous properties of the corresponding composition according to the invention are not, or not  
10 substantially, adversely affected by the intended addition.

          The composition according to the invention may be present in particular in the form of a suspension, dispersion, solution, gel, emulsion,  
15 particularly an oil-in-water (O/W) or water-in-oil (W/O) emulsion, or multiple (W/O/W or polyol/O/W or O/W/O) emulsion, in the form of a cream, paste or mousse, a dispersion of vesicles, especially of ionic or nonionic lipids, a two-phase or multiphase lotion,  
20 or a spray, powder or paste. The composition may be anhydrous: for example, it may comprise a stick or an anhydrous paste. The composition may be a composition which is used without rinsing.

          A person skilled in the art may select the  
25 appropriate galenical form, and also the method of preparing it, on the basis of his or her general knowledge, taking into account firstly the nature of

the constituents used, especially their solubility in the vehicle, and secondly the intended application of the composition.

According to another aspect, the invention  
5 also relates to a cosmetic assembly comprising:

- i) a container delimiting at least one compartment, the said container being closed by a closing member; and
- ii) a composition disposed within the said  
10 compartment, the composition being in accordance with the invention.

The container may be in any appropriate form. It may especially be in the form of a bottle, a tube, a jar, a case, a box, a sachet or a carton.

15 The closing member may be in the form of a removable stopper, a lid, a cap, a tear-off strip or a capsule, especially of the type comprising a body attached to the container and a cover cap articulated on the body. It may also be in the form of a member for  
20 selectively closing the container, especially a pump, a valve or a flap valve.

The container may be combined with an applicator, especially in the form of a block of foam or of elastomer, a felt or a spatula. The applicator  
25 may be free (tuft or sponge) or securely fastened to a rod borne by the closing member, as described, for example, in patent US 5,492,426. The applicator may be

securely fastened to the container, as described, for example, in patent FR 2 761 959.

The product may be contained directly in the container, or indirectly. By way of example, the  
5 product may be arranged on an impregnated support, especially in the form of a wipe or a pad, and arranged (individually or in plurality) in a box or in a sachet. Such a support incorporating the product is described, for example, in patent application WO 01/03538.

10 The closing member may be coupled to the container by screwing. Alternatively, the coupling between the closing member and the container is done other than by screwing, especially via a bayonet mechanism, by snap-fastening, gripping, welding,  
15 adhesive bonding or by magnetic attraction. The term "snap-fastening" in particular means any system involving the crossing of a bead or cord of material by elastic deformation of a portion, especially of the closing member, followed by return to the elastically  
20 unconstrained position of the said portion after the crossing of the bead or cord.

The container may be at least partially made of thermoplastic material. Examples of thermoplastic materials that may be mentioned include polypropylene  
25 or polyethylene.

Alternatively, the container is made of non-thermoplastic material, especially glass or metal (or

alloy).

The container may have rigid walls or deformable walls, especially in the form of a tube or a tubular bottle.

5           The container may comprise means for distributing or facilitating the distribution of the composition. By way of example, the container may have deformable walls so as to allow the composition to exit in response to a positive pressure inside the  
10 container, this positive pressure being caused by elastic (or non-elastic) squeezing of the walls of the container. Alternatively, especially when the product is in the form of a stick, the product may be driven out by a piston mechanism. Still in the case of a  
15 stick, especially of makeup product (lipstick, foundation, etc.), the container may comprise a mechanism, especially a rack mechanism, a threaded-rod mechanism or a helical groove mechanism, and may be capable of moving a stick in the direction of the said  
20 aperture. Such a mechanism is described, for example, in patent FR 2 806 273 or in patent FR 2 775 566. Such a mechanism for a liquid product is described in patent FR 2 727 609.

The container may consist of a carton with a  
25 base delimiting at least one housing containing the composition, and a lid, especially articulated on the base, and capable of at least partially covering the

said base. Such a carton is described, for example, in patent application WO 03/018423 or in patent FR 2 791 042.

5 The container may be equipped with a drainer arranged in the region of the aperture of the container. Such a drainer makes it possible to wipe the applicator and possibly the rod to which it may be securely fastened. Such a drainer is described, for example, in patent FR 2 792 618.

10 The composition may be at atmospheric pressure inside the container (at room temperature) or pressurized, especially by means of a propellant gas (aerosol). In the latter case, the container is equipped with a valve (of the type used for aerosols).

15 The content of the patents or patent applications mentioned above is incorporated by reference into the present patent application.

The invention will now be described in more detail in the light of the following examples, which  
20 are given by way of illustration and not of limitation.

The present examples illustrate the preparation of polymers in accordance with the invention that are suitable for forming a dispersion of particles in an organic medium under consideration.

25 In these examples, following preparation of the said dispersion, the weight-average ( $M_w$ ) and number-average ( $M_n$ ) molar masses of the polymer, the

glass transition temperature of the polymer, the solids content (or dry extract) of the dispersion and the size of the polymer particles are determined.

The weight-average ( $M_w$ ) and number-average ( $M_n$ ) molar masses are determined by liquid gel-permeation chromatography (THF solvent, calibration curve established with linear polystyrene standards, refractometric detector).

The measurement of the glass transition temperature ( $T_g$ ) is performed according to standard ASTM D3418-97, by differential thermal analysis (DSC "Differential Scanning Calorimetry") on a calorimeter, over a temperature range between  $-100^\circ\text{C}$  and  $+150^\circ\text{C}$ , at a heating rate of  $10^\circ\text{C}/\text{minute}$  in 150  $\mu\text{l}$  aluminium crucibles.

The crucibles are prepared in the following manner: 100  $\mu\text{l}$  of the dispersion obtained are introduced into a 150  $\mu\text{l}$  aluminium crucible and the solvent is allowed to evaporate over 24 hours at ambient temperature and at 50% relative humidity. The operation is repeated and the crucible is then introduced into a Mettler DSC30 calorimeter.

The solids content (or dry extract), i.e. the amount of non-volatile matter, may be measured in various ways: mention may be made, for example, of the methods by oven-drying or the methods by drying by exposure to infrared radiation.

The solids content is preferably measured by heating the sample with infrared rays with a wavelength of from 2  $\mu\text{m}$  to 3.5  $\mu\text{m}$ . The substances contained in the composition that have a high vapour pressure evaporate under the effect of this radiation. Measuring the weight loss of the sample makes it possible to determine the dry extract of the composition. These measurements are performed using an LP16 commercial infrared desiccator from Mettler. This technique is fully described in the documentation for the instrument supplied by Mettler.

The measuring protocol is as follows: about 1 g of the composition is spread onto a metal cup. After introducing this cup into the desiccator, it is subjected to a nominal temperature of 120°C for an hour. The wet mass of the sample, corresponding to the initial mass, and the dry mass of the sample, corresponding to the mass after exposure to the radiation, are measured using a precision balance.

The solids content is calculated in the following manner:

$$\text{dry extract} = 100 \times (\text{dry mass/wet mass}).$$

The particle sizes may be measured by various techniques: mention may be made in particular of light-scattering techniques (dynamic and static), Coulter counter methods, sedimentation rate measurements (related to the size via Stokes' law) and microscopy.



These techniques make it possible to measure a particle diameter and, for some of them, a particle size distribution.

The sizes and size distributions of the particles in the compositions according to the invention are preferably measured by static light scattering using a commercial granulometer such as the MasterSizer 2000 from Malvern. The data are processed on the basis of the Mie scattering theory. This theory, which is exact for isotropic particles, makes it possible to determine an "effective" particle diameter in the case of non-spherical particles. This theory is described especially in the work by Van de Hulst, H.C., "Light Scattering by Small Particles", Chapters 9 and 10, Wiley, New York, 1957.

The composition is characterized by its mean "effective" diameter by volume  $D[4.3]$ , defined in the following manner:

$$D[4.3] = \frac{\sum_i V_i \cdot d_i}{\sum_i V_i}$$

in which  $V_i$  represents the volume of the particles with an effective diameter  $d_i$ . This parameter is described especially in the technical documentation of the granulometer.

The measurements are performed at 25°C on a dilute particle dispersion, obtained from the composition in the following manner: 1) dilution by a

factor of 100 with water, 2) homogenization of the solution, 3) standing of the solution for 18 hours, 4) recovery of the whitish uniform supernatant.

The "effective" diameter is obtained by taking a refractive index of 1.33 for water and a mean refractive index of 1.42 for the particles.

The invention is illustrated in more detail by the examples described below.

**Example 1:**

10 This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and the macromonomer corresponding to a polyethylene/poly-  
15 butylene copolymer (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 14 g of methyl acrylate, 10 g of acrylic acid, 16 g of macromonomer of the polyethylene/polybutylene copolymer type containing methacrylate end groups (Kraton L-1253)  
20 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the  
25 appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes,

and a mixture consisting of 130 g of methyl acrylate, 30 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour.

Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of polymer thus prepared in isododecane.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass  $M_w = 175\,294$
- number-average molecular mass  $M_n = 28\,265$
- polydispersity index ( $M_w/M_n$ ) = 6.2
- theoretical dry extract: 54.9% in isododecane
- particle size: 85 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

The grafted polymer comprises 8% by weight of macromonomer relative to the weight of the polymer.

The stability of the dispersion obtained is demonstrated by implementing the following stability protocol: 8 ml of dispersion produced are placed in a haemolysis tube and centrifuged at 4000 rpm for 15 minutes using a Jouan C100-S5 centrifuge. After 15 minutes, it is found that there is no phase separation, thereby demonstrating the dispersion is stable.

**Example 2:**

This example illustrates the preparation of a polymer forming a dispersion of particles in a silicone-based solvent, the said polymer being obtained  
5 by polymerization of methyl acrylate, acrylic acid and a monomethacryloyloxypropyl polydimethylsiloxane macromonomer having a weight-average molecular weight of 5000, sold under the name MCR-M17 by Gelest Inc.

200 g of heptane, 200 g of  
10 decamethylcyclopentasiloxane, 26 g of methyl acrylate, 14 g of monomethacryloyloxypropyl polydimethylsiloxane MCR-M17 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated to  
15 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 120 g  
20 of methyl acrylate, 40 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour. Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium.

The outcome of this distillation operation is  
25 a stable dispersion of particles of polymer thus prepared in decamethylcyclopentasiloxane.

The grafted polymer comprises 7% by weight of

macromonomer (and hence of side chains soluble in D5) relative to the weight of the polymer.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- 5 - dry extract: 50% in decamethylcyclopentasiloxane, performed by thermal balance
- glass transition: 12°C by Mettler DSC
- particle size: 170 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

10 **Example 3:**

This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and the  
15 macromonomer corresponding to a polyethylene/polybutylene copolymer (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 14 g of methyl acrylate, 10 g of acrylic acid, 16 g of macromonomer of the polyethylene/polybutylene copolymer  
20 type (Kraton L-1253) and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After  
25 15 minutes at 90°C, a change is observed in the appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating

with stirring is continued for a further 15 minutes, and a mixture consisting of 70 g of methyl acrylate, 90 g of acrylic acid and 2 g of Trigonox 21S is then added dropwise over 1 hour.

5                   Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of polymer thus prepared in isododecane.

10                   The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass  $M_w$  = not characterizable by GPC

- number-average molecular mass  $M_n$  = not

15 characterizable by GPC

- polydispersity index ( $M_w/M_n$ ) = not characterizable by GPC

- theoretical dry extract: 53.6% in isododecane

- particle size: not measured.

20                   The grafted polymer comprises 8% by weight of macromonomer relative to the weight of the polymer.

After the stability protocol has been implemented in accordance with Example 1, the dispersion obtained is found to be stable.

25   Example 4:

This example illustrates the preparation of a polymer forming a dispersion of particles in a carbon-

based solvent, the said polymer being obtained by polymerization of methyl acrylate, acrylic acid and the macromonomer corresponding to a polyethylene/polybutylene copolymer with methacrylate end groups  
5 (Kraton L-1253).

200 g of heptane, 200 g of isododecane, 28 g of methyl acrylate, 12 g of macromonomer of the polyethylene/polybutylene copolymer type with methacrylate end groups (Kraton L-1253) and 3.2 g of  
10 tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

The reaction mixture is stirred and heated at ambient temperature to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the  
15 appearance of the reaction medium, which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 150 g of methyl acrylate, 10 g of acrylic acid and 2 g of Trigonox 21S is then  
20 added dropwise over 1 hour.

Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium. The outcome of this distillation operation is a stable dispersion of particles of  
25 polymer thus prepared in isododecane.

The grafted polymer comprises 6% by weight of macromonomer relative to the weight of the polymer.

The characteristics of the polymer and of the particles formed by the said polymer are as follows:

- weight-average molecular mass  $M_w = 143\ 639$
- number-average molecular mass  $M_n = 23\ 965$
- 5 - polydispersity index ( $M_w/M_n$ ) = 5.99
- theoretical dry extract: 51.3% in isododecane
- particle size: 48 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

After the stability protocol has been  
10 implemented in accordance with Example 1, the dispersion obtained is found to be stable.

**Example 5:**

This example illustrates the preparation of a polymer forming a dispersion of particles in a silicone  
15 oil, the said polymer being obtained by polymerization of methyl acrylate and a monomethacryloyloxypropyl polydimethylsiloxane macromonomer having a weight-average molecular weight of 5000, sold under the name MCR-M17 by Gelest Inc.

20           200 g of heptane, 200 g of decamethylcyclopentasiloxane, 30 g of methyl acrylate, 10 g of monomethacryloyloxypropyl polydimethylsiloxane MCR-M17 and 3.2 g of tert-butyl peroxy-2-ethylhexanoate (Trigonox 21S) are loaded into a 1 litre reactor.

25           The reaction mixture is stirred and heated to 90°C over 1 hour. After 15 minutes at 90°C, a change is observed in the appearance of the reaction medium,



which passes from a transparent appearance to a milky appearance. Heating with stirring is continued for a further 15 minutes, and a mixture consisting of 160 g of methyl acrylate and 2 g of Trigonox 21S is then  
5 added dropwise over 1 hour. Next, the mixture is heated for 4 hours at 90°C and the heptane is then distilled from the reaction medium.

The outcome of this distillation operation is a stable dispersion of particles of polymer thus  
10 prepared in decamethylcyclopentasiloxane (D5).

The grafted polymer comprises 5% by weight of macromonomer (and hence of side chains soluble in D5) relative to the weight of the polymer.

The characteristics of the polymer and of the  
15 particles formed by the said polymer are as follows:

- weight-average molecular mass  $M_w = 102\,347$
- number-average molecular mass  $M_n = 28\,283$
- polydispersity index ( $M_w/M_n$ ) = 3.62
- dry extract: 51.4% in D5, performed by thermal  
20 balance
- glass transition: 12°C by Mettler DSC
- particle size: 160 nm with polydispersity of 0.04, performed on a Malvern Autosizer Lo-C at 25°C.

After the stability protocol has been  
25 implemented in accordance with Example 1, the dispersion is found to be stable.

The polymers of Examples 1 to 5 comprise the

following monomers, their amounts being indicated as a percentage by weight of the polymer:

Polymer	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Methyl acrylate	72	73	42	89	95
Acrylic acid	20	20	50	5	0
Carbon-based macromonomer	8	-	8	6	-
Silicone-based macromonomer	-	7	-	-	5

5 Examples 6 to 10:

5 foundations were prepared, having the following compositions (the amounts are indicated as a percentage relative to the total weight of the composition):

10

Examples	6	7	8	9	10
Abil EM 97	1.8	1.8	1.8	1.8	1.8
Inwitor 780 K	0.6	0.6	0.6	0.6	0.6
Isododecane	20.38	22.10	20.28	20.11	22.10
D5	10	7.9	10	10	7.95
Grafted polymer dispersion	Ex. 1 3.82	Ex. 2 4.20	Ex. 3 3.92	Ex. 4 4.09	Ex. 5 4.15
Pigments	10	10	10	10	10
Silicone gum	3	3	3	3	3
Nylon powder	8	8	8	8	8
Water	41.4	41.4	41.4	41.4	41.4
Preservative	0.3	0.3	0.3	0.3	0.3
Magnesium sulfate	0.7	0.7	0.7	0.7	0.7

Each composition contains 2.1% by weight of active grafted polymer substance.

Ingredients used:

ABIL EM 97:  $\alpha,\omega$ -substituted, ethoxylated propoxylated silicone/cyclomethicone (85/15) blend, sold by the Goldschmidt Company

- 5 Inwitor 780 K: mono- and diglycerides of isostearic acid esterified with succinic acid sold by the Sasol Company

D5: cyclopentasiloxane

- Silicone gum: blend of polydiphenyl dimethylsiloxane  
10 and cyclopentasiloxane (15/85) sold under the name Mirasil C (DPDM by Rhodia)

Nylon powder sold under the name Orgasol<sup>®</sup> 2002 extra D NAT COS by Atofina

the 10% of pigments comprise:

- 15 1.43% of yellow iron oxides coated with triisopropyl isostearoyl titanate (BYO-I 2 from Kobo)  
0.46% of brown iron oxides coated with triisopropyl isostearoyl titanate (BRO-I 2 from Kobo)  
0.22% of black iron oxides coated with triisopropyl  
20 isostearoyl titanate (BBO-I 2 from Kobo)  
7.89% of titanium dioxide coated with triisopropyl isostearoyl titanate (BTD-401 from Kobo)

- Thereafter the transfer index of each composition was measured in the presence of sebum in  
25 accordance with the measurement protocol described above. The results obtained were as follows:

Example	6	7	8	9	10
Transfer index	0.5	0.5	0.5	3.5	3.5

It is found that the compositions have a transfer index in the presence of sebum of less than 4.

Furthermore, the compositions of Examples 6 to 8 have a better transfer resistance in the presence of sebum than the compositions of Examples 9 and 10. It is therefore observed that the presence of acrylic acid in the grafted polymer promotes the non-transfer property of the deposit obtained with the composition.